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<b>(54) Title:</b> A METHOD FOR INHIBITING GAS HYDRATE FORMATION  <b>(57) Abstract</b>  The invention relates to a method for inhibiting the formation, growth and/or agglomeration of gas hydrate crystals in a mixture containing low-boiling hydrocarbons and water, characterized by adding to the mixture an effective amount of at least one additive selected from the group of polymers and copolymers of N-vinyl-2-pyrrolidone, and mixtures thereof. Optionally, a film-forming compound is also added.		

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## A METHOD FOR INHIBITING GAS HYDRATE FORMATION

This invention relates to a process for inhibiting the formation of gas hydrates in systems containing low-boiling hydrocarbons and water.

Low-boiling hydrocarbons, such as methane, ethane, propane, butane and iso-butane, are present in natural gas and also in crude oil. Since water is also present in varying amounts, the mixture of low-boiling hydrocarbons and water (such as present in natural gas), under conditions of elevated pressure and reduced temperature, tends to form hydrate crystals (gas hydrate crystals). The maximum temperature at which hydrates can be formed strongly depends on the pressure of the system. For example, ethane at a pressure of approximately 1MPa can form hydrates at temperatures below 4 °C whereas at a pressure of 3MPa stable hydrates can be present at temperatures lower than 14 °C. With respect to this strong dependence of the hydrate melting point on pressure, hydrates markedly differ from ice. As described by M. von Stackelberg and H.R. Muller (Z. Electrochem. 1954 58 25 ), methane and ethane hydrates form cubic lattices having a lattice constant of 1.2 nm (hydrate structure I). The lattice constant of the (also) cubic propane and butane gas hydrates is 1.73 nm (hydrate structure II). However, the presence of even small amounts of propane in a mixture of low-boiling hydrocarbons will result in the formation of gas hydrates having structure II (J.H. van der Waals and J.C. Platteeuw, Adv. Chem. Phys. 2 1959 1).

It has been known for a long time, that gas hydrate crystals, when allowed to form and grow inside a conduit such as a pipeline, tend to block or even damage the conduit. To prevent such blocking, the following thermodynamic measures are possible in principle: removal of free water, maintaining elevated temperatures and/or reduced pressures or the addition of melting point depressants (antifreeze). In practice, in most cases the last-mentioned measure

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is applied. However, the antifreezes, such as the lower alcohols and glycols, have to be added in substantial amounts (of the order of 30 per cent by weight of the water present) to be effective. An additional disadvantage of such amounts is that recovery of the added antifreezes is usually required during further processing of the mixture.

An attractive alternative to the anti-hydrate measures described above, in particularly the antifreezes, is to use a crystal growth inhibitor. The principle of interfering with crystal growth is known. In relation to gas hydrates this principle is suggested in EP-A-309210, which is directed to a method for preventing flow stoppage of a wet gas stream by incorporating therein a surface-active agent which inhibits the formation of gas hydrates and/or the agglomeration of gas hydrate crystallites into large crystalline masses. As surface-active agents there are mentioned in this document organic phosphonates, phosphate esters, phosphonic acids, salts and esters of phosphonic acids, inorganic polyphosphates, salts and esters of inorganic polyphosphates, polyacrylamides and polyacrylates. However, in the single example of EP-A-309210 no actual evidence is given for the effectivity of the single surface-active agent, hydroxyl amine phosphate, used therein.

Plants and poikilothermic animals such as insects and cold-water fish are known to protect themselves from freezing, both by antifreezes such as glycols and by special peptides and glycopeptides (termed Antifreeze Proteins, AFP's and Antifreeze Glycoproteins, AFGP's) which interfere with ice crystal growth (A.L. de Vries, Comp. Biochem. Physiol. 73 1982 627). The present applicants found such cold-water fish peptides and glycopeptides also to be effective in interfering with the growth of gas-hydrate crystals. However, their production and use for this purpose are currently considered to be uneconomical.

Poly-N-vinyl-2-pyrrolidone (Polyvinyl pyrrolidone, PVP) is a well-known water-soluble polymer, currently used in particular in pharmacy. PVP is known to interfere with the growth of different

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crystals, such as the crystal growth of several drugs in aqueous suspension (K.H. Ziller and H.H. Ruppert, Pharm. Ind. 52 1990 1017), and also with the growth of ice crystals. However, in suppressing the growth of ice crystals PVP has been noted to be much less effective than the glycoproteins isolated from dialysed blood serum of the antarctic fish *Notothenia neglecta* (F. Frank et al. Nature 325 1987 146). Also, as an additive to the antifreeze butane 2,3,-diol, PVP has been noted (R.L. Sutton, J.Chem. Soc. Faraday Trans. 87 1991 3747) to be less effective on ice crystal growth than polyethylene glycol (PEG).

It has now been found that compounds belonging to the group of polymers and copolymers of N-vinyl-2-pyrrolidone and mixtures thereof are very effective, in relatively low concentrations, in interfering with the growth of gas-hydrate crystals, and therefore that they can be useful in inhibiting the plugging of conduits containing low-boiling hydrocarbons and water.

The invention therefore relates to a method for inhibiting the formation, growth and/or agglomeration of gas hydrate crystals in a mixture containing low-boiling hydrocarbons and water, characterized by adding to the mixture an effective amount of at least one additive selected from the group of polymers and copolymers of N-vinyl-2-pyrrolidone, and mixtures thereof.

A preferred group of additives according to the invention are the homopolymers of N-vinyl-2-pyrrolidone (PVP). These are available commercially, e.g. from BSA under the trade name KOLIDON, in average molecular weights ranging from about 5000 daltons (K12) or less to about 400000 daltons (K90) and more. In general the present inventors found the lower molecular weight PVP's, especially those of between 5000 and 40000 daltons, to be the more effective in inhibiting the formation of gas hydrate crystals.

Possible copolymers for use as additives according to the invention, which are available commercially, are the copolymers of N-vinyl-2-pyrrolidone with 1-butene, with 1-hexene, with 1-decene, with vinyl chloride, with vinyl acetate, with ethyl acrylate, with 2-ethylhexyl acrylate, and with styrene. Copolymers of

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N-vinyl-2-pyrrolidone with mixtures of the above can also be used. Preferably, the copolymers for use according to the invention will contain at least 30 mol% of the N-vinyl-2-pyrrolidone component.

5 The amount of additive according to the invention is generally between 0.05 and 4 wt%, preferably between 0.25 and 1 wt%, based on the amount of water in the hydrocarbon-containing mixture.

The additives according to the invention can be added to the subject mixture of low-boiling hydrocarbons and water, as their dry powder or, preferably, in concentrated aqueous solution.

10 While the polymers and copolymers according to the invention interfere effectively with the growth of hydrate crystals, it may be advantageous also to interfere with agglomeration of any remaining crystallites and with their adhesion to the wall of the conduit. For this purpose film-formers, which are known to prevent  
15 water-wetting of metal surfaces, can be added.

Typical examples of such film-formers are long-chain alkyl amines, alkyl diamines and imidazolines, optionally in combination with high molecular-weight organic acids.

Also suitable as film-formers are monovalent, but preferably  
20 divalent, salts of long-chain alkarylsulphonic acids. These are subject of the present applicant's EP-A-457375.

The following Examples will illustrate the invention.

Example 1

In this example, an aqueous solution of tetrahydrofuran (THF)  
25 was used as a model for wet gas, since tetrahydrofuran in water is known to form hydrate (structure II) crystals at about the same temperature as wet gas, but already at atmospheric pressure - for example, an 18.9 wt% aqueous solution of THF has a hydrate melting point of 4.3 °C at atmospheric pressure (S.R. Couch and D.W.  
30 Davidson, Can. J. Chem. 49 1971 2691).

The effect of different additives on the growth of a single hydrate crystal was studied by adding 0.5 wt% of additive to a solution of 18.9 wt% THF in water (approx. molar ratio 1:17), also containing 3 wt% of NaCl, and performing the experiments described  
35 below.

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A glass vessel, open to atmospheric pressure and containing the solution to be tested is immersed in a thermostatically controlled bath. After thermal equilibrium has been reached, a capillary holding a small ice crystal (about 0.1 gram) is introduced into the solution. In the reference solution, not containing the additives according to the invention, this introduction of a small ice crystal seeds the growth of large type II hydrate crystals which are easy to inspect visually. The morphology and weight of the hydrate crystals formed during 195 minutes at 0 °C, followed by 16.5 hours at +0.4 °C, after the introduction of the capillary into the different solutions are determined and compared.

It was observed, that under the above experimental conditions hydrate crystals grown in the reference solution (not containing additives) had a distinct and regular appearance. At the beginning of crystal growth geometrically perfect hexagonal plates were frequently observed, while at later stages the crystals acquired pyramidal shapes, the angles between the faces of the pyramids being 70.9 (+/- 1.9) degrees. In all cases flat crystal planes intersected in sharp angles.

The following additives, not according to the invention, were added in an amount of 0.5 wt% to the reference solution and investigated under the above experimental conditions:

- Polyethylene glycol (MW 35000, supplier Fluka)
- Polypropylene glycol (P2000, visc. 500 mPa.s at 20 °C, supplier Fluka)
- Polyacrylamide (MW 5000000-6000000, supplier Janssen Chimica)
- Polyacrylic acid (MW 5000, supplier Janssen Chimica)
- Polyvinylalcohol (MW 100000, supplier Fluka)
- Ethyleneimine polymer (MW 600000-1000000, supplier Fluka)
- Polyanethol sulfonic acid sodium salt (supplier Fluka)
- Carboxymethylcellulose sodium salt (visc. of 2% aq. solution 400-800 mPa.s at 25 °C, supplier Sigma Chemicals)
- Methylcellulose (visc. of 2% aq. solution 1500 and 4000 mPa.s at 25 °C, supplier Sigma Chemicals)

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- Hydroxyethylcellulose (Trade name Natrosol 250HHR-P, supplier Hercules)

5 None of these additives significantly altered the shape or size of the hydrate crystals formed, compared to the reference solution.

By contrast, the addition of 0.5 wt% of one of several PVP's, or of a 1:1 copolymer of 1-butene with N-vinylpyrrolidone (trade name AGRIMER AL-904 of GAF chemicals corporation, Wayne, NJ, mean molecular weight approximately 16000), resulted under the above  
10 experimental conditions in the growth of severely deformed and much smaller hydrate crystals. The crystals had the appearance of a sheet of paper crushed into a ball. PVP K15 (mean molecular weight approximately 10000) resulted in rounded edges between the crystal planes, to such an extent that flat crystal faces were barely  
15 visible. PVP K90 (mean molecular weight approximately 400000), as well as the copolymer, resulted in no flat crystal faces being visible.

The experimental set-up and the appearance of the grown crystals are shown schematically in Figure 1, wherein 1 is the  
20 thermostatically controlled bath, 2 the solution to be tested, 3 the capillary, 4 the ice crystal seed, 5 a hydrate crystal grown in the THF/NaCl solution without additive and 6 a hydrate crystal grown in the THF solution containing 0.5 wt% of PVP K90.

25 The following weights of (single) hydrate crystals were found in the different solutions, after 195 minutes at 0 °C followed by 16.5 hours at +0.4 °C:

-Reference solution without additive	27.6 grams
-Reference solution with 0.5 wt% Polyacrylamide	30.3 grams
-Reference solution with 0.5 wt% PVP K15	6.4 grams
30 -Reference solution with 0.5 wt% PVP K25	2.0 grams
-Reference solution with 0.5 wt% PVP K30	1.5 grams
-Reference solution with 0.5 wt% PVP K90	0.7 grams
-Reference solution with 0.5 wt% PVP AGRIMER	0.0 grams



Example 2

In this example, field conditions were simulated in an experimental set-up as schematically shown in Figure 2, comprising a two-liter stirred high-pressure autoclave 11 connected via a gear pump 12 to a coiled copper pipeline 13 of 16 m length and 6 mm internal diameter which is immersed in a thermostatically controlled bath 14. The pressure difference between the inlet and outlet of the pipeline is continuously monitored by a differential pressure transmitter 15.

10       The autoclave was loaded at 13 °C with 400 ml of demineralised water (in which additives could be dissolved and with 800 ml of Shellisol D60 (trade name), a mixture of paraffinic and naphthenic hydrocarbons mainly in the  $C_{10}$  -  $C_{12}$  range. In addition the autoclave was loaded with ethane until the pressure (at 13 °C) within the autoclave was 20 bara. After loading and closing the autoclave, the stirred mixture was circulated through the system at a rate of 6.1 liters/hour. The temperature of the bath was lowered gradually, at a rate of 5 °C per hour. To initiate the formation of hydrates, a piece of dry ice (solid  $CO_2$ ) was continuously held against the inlet of the coiled pipeline. During the gradual cooling stage the pressure drop over the coiled pipeline and the temperature of the bath were continuously monitored as a function of time.

25       The temperature at which the pressure drop between the inlet and outlet of the coiled pipeline exceeded 1 bar was considered to be the blocking temperature.

The following blocking temperatures were found, in a system loaded as described above, with and without the addition of small amounts of different additives.

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	No additive added	8.4 °C
	2 grams (0.5 wt%) of polyacrylamide	8.8 °C
	2.0 grams (0.5 wt%) of PVP K90	3.3 °C
	0.2 grams (0.05 wt%) of PVP K90.	7.4 °C
5	2.0 grams (0.5 wt%) of PVP K15	0.6 °C
	0.4 grams (0.1 wt%) of PVP K15	2.8 °C
	2.0 grams (0.5 wt%) of AGRIMER	1.3 °C

The weight percentages in the above list refer to the amount of water present in the load.

10 Example 3

In this experiment a mixture of natural gas, condensate and water was produced from a well and transported through a pipeline of 0.0762 m internal diameter and 2414 m length. Natural gas was produced at a rate of  $56.6 \times 10^3 \text{ m}^3/\text{day}$ , condensate at a rate of  $3.18 \text{ m}^3/\text{day}$  and water at a rate of  $0.318 \text{ m}^3/\text{day}$ . The hydrate-temperature of the mixture, which is the temperature below which hydrates will form if no hydrate inhibitor is added, was approximately 10 °C, and the mixture was transported through the pipeline at a temperature of 1 °C. To retard hydrate formation in the line 0.5 wt% PVP K17 was added to the mixture at the upstream side thereof. It was found that during a period of approximately 17 hours after start of transportation through the line no significant pressure drop occurred within the pipeline along the length thereof. Thereafter hydrate formation in the line caused a gradually increasing pressure drop, until complete blocking of the line at approximately 37 hours after start of transportation. If no PVP would have been added to the mixture, hydrate formation would have caused complete blocking of the line within a much shorter period.

C L A I M S

1. A method for inhibiting the formation, growth and/or agglomeration of gas hydrate crystals in a mixture containing low-boiling hydrocarbons and water, characterized by adding to the mixture an effective amount of at least one additive selected from the group of polymers and copolymers of N-vinyl-2-pyrrolidone, and mixtures thereof.
2. A method according to claim 1, characterized in that the additive is a poly-N-vinyl-2-pyrrolidone (PVP)
3. A method according to claim 2, characterized in that the PVP is of a molecular weight between 5000 and 1000000 daltons.
4. A method according to claim 3, characterized in that the PVP is of a molecular weight between 5000 and 40000 daltons.
5. A method according to claim 1, characterized in that the additive is a copolymer of N-vinyl-2-pyrrolidone with one or more other monomer(s) selected from the group of 1-butene, 1-hexene, 1-decene, vinylchloride, vinyl acetate, ethyl acrylate, 2-ethylhexyl acrylate and styrene.
6. A method according to claim 1 or 5, characterized in that the copolymer contains at least 30 mol% of the N-vinyl-2-pyrrolidone element in the polymeric chain.
7. A method according to any one of claims 1-6, characterized in that a concentration of between 0.05 and 4 wt% of the additive, based on the water content, is added to the hydrocarbon/water mixture.
8. A method according to claim 7, characterized in that the concentration of the additive is between 0.25 and 1 wt%.
9. A method according to any one of claims 1-8, characterized in that a film-forming compound is also added.
10. A method according to claim 9, characterized in that the film-forming compound is chosen from the group of long-chain alkyl amines, alkyl diamines and imidazolines, optionally in combination

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with high molecular-weight organic acids, or from the group of monovalent, but preferably divalent, salts of long-chain alkarylsulphonic acids.

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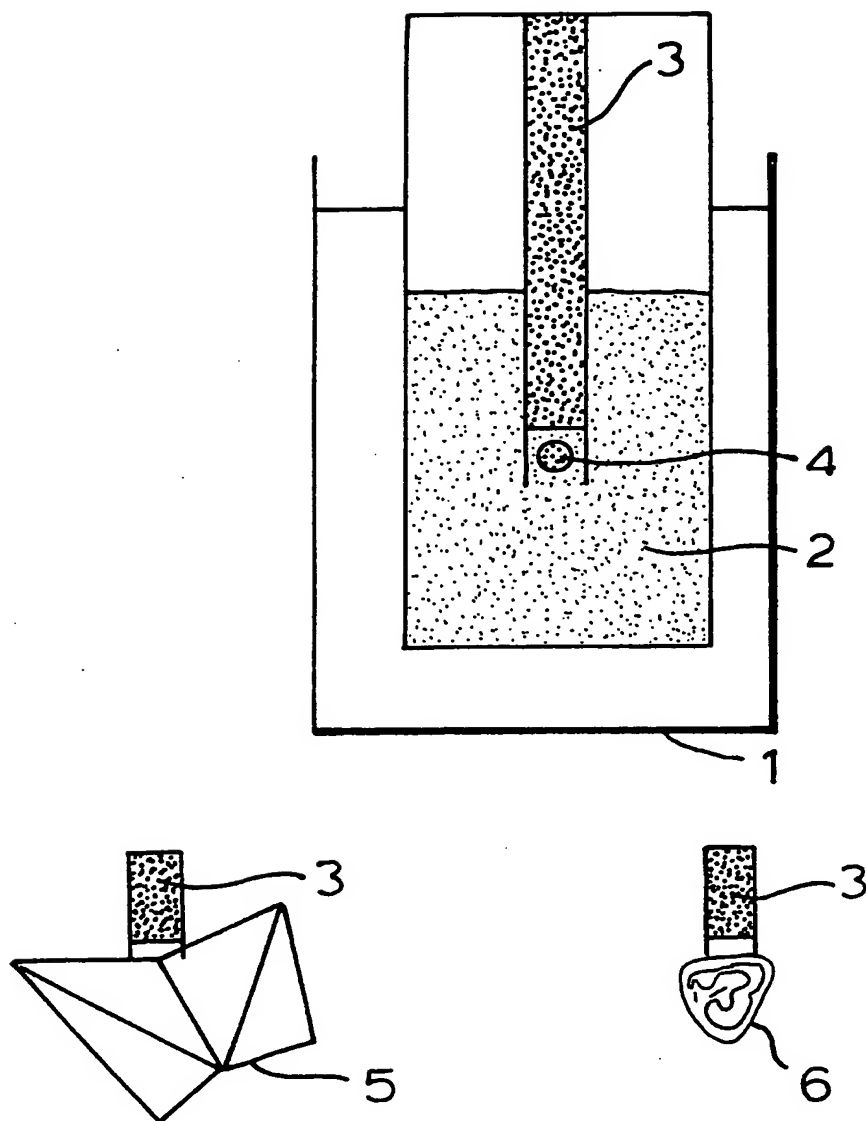


FIG. 1

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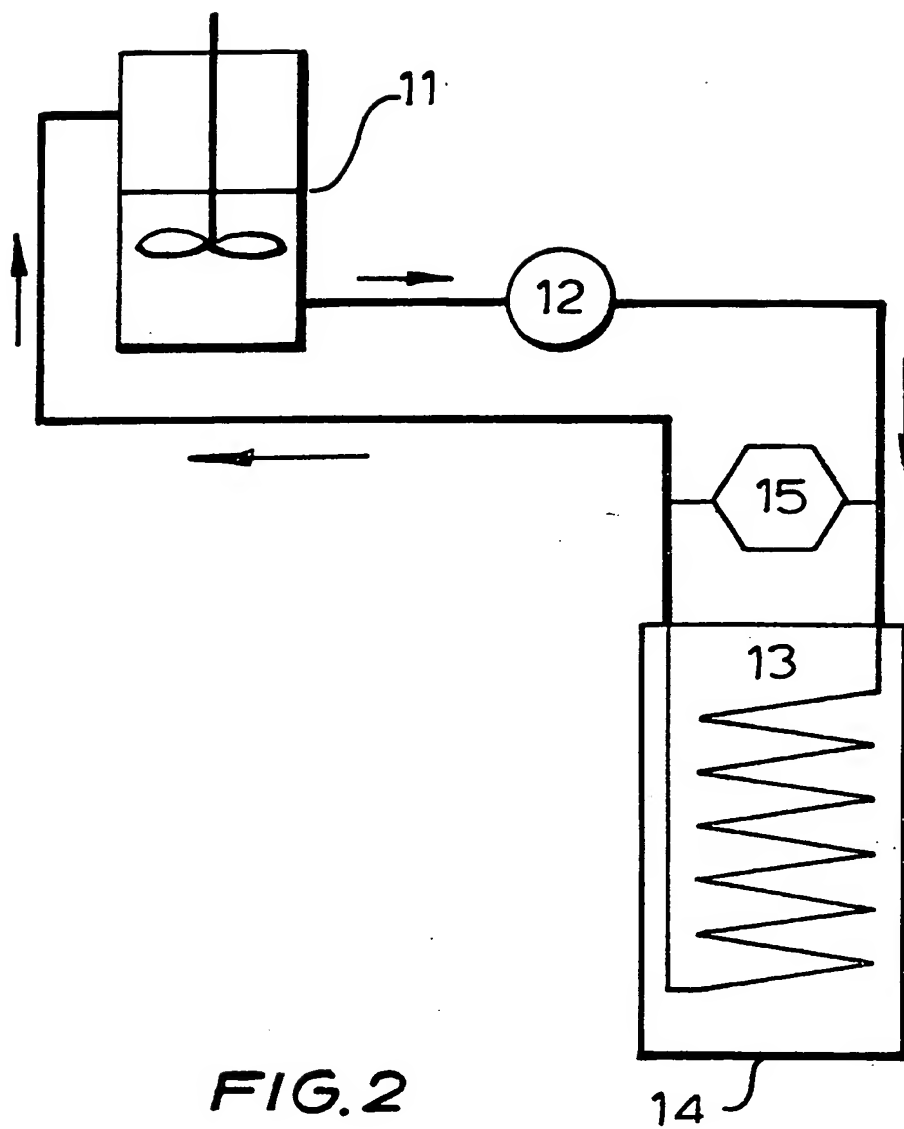


FIG. 2

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/01519

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 E21B37/06; C10L3/00; F17D1/02; C07C7/20 F15D1/00		
<b>II. FIELDS SEARCHED</b>		
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Classification System	Classification Symbols	
Int.Cl. 5	E21B ; F17D ; F15D ; C09K C07C ; C10L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	FR,A,2 618 876 (I.F.P.) 3 February 1989 see the whole document	1-10
A	US,A,3 962 110 (TATE) 8 June 1976 see the whole document	1-10
A	US,A,4 792 412 (HEILWEIL) 20 December 1988 see the whole document	1-10
A	US,A,4 663 408 (SCHULZ ET AL.) 5 May 1987 see the whole document	1-10
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<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
04 OCTOBER 1993		18. 10. 93
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,3 290 883 (GILES ET AL.) 13 December 1966 see the whole document ---	1-10
A	FR,A,1 390 134 (BASF) 11 February 1965 see the whole document ---	1-10
A	US,A,3 015 546 (MICHAELS ET AL.) 2 January 1962 see the whole document ---	1-10
A	FR,A,1 245 512 (ESSO) 3 October 1960 see the whole document ---	1-10
A	FR,A,1 258 482 (ESSO) 6 March 1961 see the whole document ---	1-10
A	CA,A,658 216 (ESSO) 19 February 1963 see the whole document -----	1-10



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SA 75371

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2618876	03-02-89	None	
US-A-3962110	08-06-76	AU-B- 450737 AU-A- 3460171 CA-A- 977543 DE-A- 2151564	18-07-74 19-04-73 11-11-75 20-04-72
US-A-4792412	20-12-88	None	
US-A-4663408	05-05-87	None	
US-A-4489180	18-12-84	CA-A- 1225184 DE-A- 3439797 US-A- 4970260	04-08-87 09-05-85 13-11-90
US-A-3290883		None	
FR-A-1390134		NL-A- 6404637	28-10-64
US-A-3015546		DE-B- 1101854 GB-A- 857754	
FR-A-1245512		BE-A- 570325 BE-A- 570373 DE-B- 1250950 DE-A- 1420867 DE-A- 1444817 FR-E- 75217 FR-E- 76478 GB-A- 808665 NL-C- 102717 US-A- 3137679	17-04-69 23-03-72
FR-A-1258482		None	
CA-A-658216		None	

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